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(71)Applicant : FUJI PHOTO FILM CO LTD

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(72)Inventor : KAGAWA OKIMASA
MAEKAWA YUKIO

(54) NONAQUEOUS SECONDARY BATTERY

(57)Abstract:

PURPOSE: To provide a nonaqueous secondary battery constituted of a positive electrode active material, a negative electrode material, and a nonaqueous electrolyte containing light metal salt, having a high discharge potential and a high capacity, and excellent in safety and charge/discharge cycle characteristics by adding a specific material as a conductive agent for a positive electrode and/or a negative electrode mixture.

CONSTITUTION: One or more carbon/ceramic composite materials preferably constituted of carbon and one or more of a carbide, a boride, an oxide, and a nitride are contained in a conductive agent for a positive electrode and/or negative electrode mixture. A carbide of one or more of Si, Co, Zr, W, Ge, Ta, Ti, Fe, Nb, Ni, V, Hf, and Mo; a boride of one or more of Si, Zr, W, Ta, Ti, Nb, La, and Mo; an oxide of one or more of Al, Si, Mg, and Zr; and a nitride of one or more of Si, Co, Zr, W, Ge, Ta, Ti, Fe, Nb, Ni, V, Hf, Mn, Sn, In, Ga, and Mo are preferably used.

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CLAIMS

[Claim(s)]

- [Claim 1] the non-water rechargeable battery which consists of a positive active material, negative-electrode material, and nonaqueous electrolyte containing a light metal salt -- being related -- a positive electrode and/or a negative electrode -- the non-water rechargeable battery characterized by including a kind of carbon / ceramic composite material at least as an electric conduction agent of a mixture
- [Claim 2] The non-water rechargeable battery according to claim 1 characterized by this carbon / ceramic composite material being the composite material which consists of at least a kind of carbide, a way ghost, an oxide, and a nitride with carbon.
- [Claim 3] The non-water rechargeable battery according to claim 1 characterized by this carbon / ceramic composite material being the composite material which consists of carbide of at least carbon, a kind of silicon, cobalt, a zirconium, a tungsten, germanium, a tantalum, titanium, iron, niobium, nickel, vanadium, a hafnium, and molybdenum.
- [Claim 4] The non-water rechargeable battery according to claim 1 characterized by this carbon / ceramic composite material being the composite material which consists of at least carbon, a kind of silicon, a zirconium, a tungsten, a tantalum, titanium, niobium, a lanthanum, and a way ghost of molybdenum.
- [Claim 5] The non-water rechargeable battery according to claim 1 characterized by this carbon / ceramic composite material being the composite material which consists of an oxide of carbon, at least a kind of aluminum and silicon, magnesium, and a zirconium.
- [Claim 6] The non-water rechargeable battery according to claim 1 characterized by this carbon / ceramic composite material being the composite material which consists of a nitride of at least carbon, a kind of silicon, cobalt, a zirconium, a tungsten, germanium, a tantalum, titanium, iron, niobium, nickel, vanadium, a hafnium, manganese, tin, an indium, a gallium, and molybdenum.
- [Claim 7] This negative-electrode material is MZ-pGO-qX (the semimetal element of the 13-15th groups of a periodic table in connection with occlusion discharge of a lithium ion and transition metals of MZ being independent here or ***** which consists of those combination is chalcogenide, GO(s) are the so-called amorphous mesh formation agent with being stable for making it amorphous, and a mesh ornamentation agent, and X is a halogen.). ***** in connection with lithium occlusion discharge in p expresses the mole ratio of chalcogenide and an amorphous mesh formation agent, and it is 0.25-5.0, and ***** in connection with lithium occlusion discharge in q expresses the mole ratio of chalcogenide and a halogen, and it is 0-1 it is -- non-water rechargeable battery according to claim 1 characterized by being this amorphous negative-electrode material
- [Claim 8] The non-water rechargeable battery according to claim 1 with which this light metal salt is characterized by containing lithium salt.
- [Claim 9] The non-water rechargeable battery according to claim 1 with which the solvent of this nonaqueous electrolyte is characterized by containing ethylene carbonate.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Industrial Application] this invention relates to the non-water rechargeable battery which improved charge-and-discharge capacity.

[0002]

[Description of the Prior Art] If negative-electrode material is carried out and they are used for non-water rechargeable batteries although a lithium metal and a lithium alloy are typical, into charge and discharge, a lithium metal will grow up to be arborescence and will carry out internal short-circuit, or the activity of the arborescence metal itself is high, and risk of igniting is entailed. On the other hand, it has come to put in practical use occlusion and nature material of a baked carbon which can be emitted for a lithium recently. Since conductivity has itself, the fault of this carbonaceous material is a lithium metal's depositing on carbonaceous material in the case of a surcharge or boosting charge, and depositing an arborescence lithium metal after all. Although the method of lessening the amount of positive active materials and preventing a surcharge is adopted in order to avoid this, since the amount of the active material matter is limited, service capacity will be restricted by this method. Moreover, since carbonaceous material has comparatively small specific gravity, service capacity will be restricted in a double meaning called a low in the capacity per volume. Using oxides, such as V, Si, B, Zr, and Sn, and those multiple oxides for negative-electrode material is proposed as what, on the other hand, attains a non-water rechargeable battery with a 3-3.6V class high discharge potential (JP, 5-174818, A, this 6- 60867, this 6- 275268, this 6- 325765, this 6- 338325, EP- 615296). oxides, such as these [V, Si, B Zr, and Sn], and those multiple oxides combine with a certain kind of positive electrode -- 3-3.6 -- the big non-water rechargeable battery of service capacity is given by Class V, and dendrite generating is almost lost Since it had high service capacity and the outstanding room temperature cycle property, although the non-water rechargeable battery which makes these carbonaceous material, and oxides, such as V, Si, B, Zr, and Sn, and those multiple oxides negative-electrode material was a cell expected as a power supply for portable devices of the next generation, it had the practical big problem that a cycle property fell sharply, at the operation temperature of 40 degrees C or more.

[0003]

[Problem(s) to be Solved by the Invention] The first technical problem of this invention is obtaining the non-water rechargeable battery which had a high discharge potential and was excellent in the safety of high capacity. The second technical problem of this invention is obtaining the non-water rechargeable battery with which the cycle property beyond a room temperature was improved.

[0004]

[Means for Solving the Problem] the non-water rechargeable battery with which the technical problem of this invention consists of a positive active material, negative-electrode material, and nonaqueous electrolyte containing a light metal salt -- being related -- an electrode -- it was attained by the non-water rechargeable battery characterized by including carbon and ceramic composite material (composite material which serves as carbon from a kind of carbide, a way ghost, an oxide, and a nitride at least preferably) in a mixture

[0005] positive and the negative electrode of the non-water rechargeable battery of this invention -- a positive electrode -- a mixture or a negative electrode -- a mixture can be painted on a charge collector and can be made a positive electrode or a negative electrode -- a positive active material or negative-electrode material, carbon / ceramic composite material and other electric conduction agents, a binder, a filler, a dispersant, an ion electric conduction agent, a pressure reinforcement agent, and an additive are used for a mixture, respectively

[0006] The carbon / ceramic composite material used by this invention are composite material which serves as carbon from a kind of carbide, a way ghost, an oxide, and a nitride at least.

[0007] As a carbon material used for composite-ization, carbon black, such as graphite, such as natural graphites (a phosphorus flaky graphite, earthy graphite, etc.) and an artificial graphite, petroleum coke, pitch coke, coal, a cresol-resin baked carbon, a furan-resin baked carbon, a polyacrylonitrile fiber baked carbon, a vapor-growth graphite, vapor-growth carbon, a mesophase pitch baked carbon, acetylene black, KETCHIEN black, channel black, lamp black, and thermal black, is mentioned.

[0008] As a carbon material and carbide which can carry out [****]-izing, even if there is little each carbide of silicon, cobalt, a zirconium, a tungsten, germanium, a tantalum, titanium, iron, niobium, nickel, vanadium, a hafnium, and molybdenum, a kind can be mentioned. The examples of a compound of carbide are SiC, Co₂C, CoC₂, ZrC, W₂C WC, TaC and TiC, Fe₃C, NbC, NiC and VC, V₄C₃, V₅C, B₄C, HfC, Mo₂C, and MoC, and independent ** can compound and use these. As a way ghost which can carry out [****]-izing to a carbon material, even if there are few silicon, a zirconium, a tungsten, a tantalum, titanium, niobium, lanthanums, and each way ghosts of molybdenum, a kind can be mentioned. The examples of a compound of a way ghost are Si₂B, SiB, SiB₃, SiB₄, ZrB₂, WB, TaB₂, TiB₂, LaB₆, and MoB, and independent ** can compound and use these. As an oxide which can carry out [****]-izing to a carbon material, even if there is little each oxide of aluminum, silicon, magnesium, and a zirconium, a kind can be mentioned. the example of a compound of an oxide -- aluminum₂ -- O₃, SiO₂, MgO, and ZrO₂ it is -- independent ** can compound and use these As a nitride which can carry out [****]-izing to a carbon material, even if there is little each nitride of silicon, cobalt, a zirconium, a tungsten, germanium, a tantalum, titanium, iron, niobium, nickel, vanadium, a hafnium, manganese, tin, an indium, a gallium, and molybdenum, a kind can be mentioned. The example of a compound of a nitride SiN, Si₂N₃, Si₃N₄, Co₂N, Co₃N₄, ZrN, W₂N, WN₂, W₂N₃, germanium₃N₄, TaNTiN, Fe₂N, Fe₄N, NbN, nickel₃N, VN, HfN, Mn₄N, Mn₂N, Mn₃N₂, SnNiN, GaN, It is MoN and Mo₂N, and independent ** can compound and use these.

[0009] As a method of manufacturing carbon and ceramic composite material, there are the coating method, the kneading method, a

sintering process, the mixed grinding method, etc., and the optimal manufacture method is chosen according to the kind of ceramic material used for composite-ization. Generally as a coating method, "the chemical vapor deposition (CVD)" which the reaction or decomposition of material gas generates [chemical vapor deposition] ceramic material, and deposits a carbon front face, and the "converting method" which the surface section of a carbon material is made to react with an oxide at an elevated temperature, and is used as carbide are performed. In addition, the kneading method kneads binders, such as a tar pitch and synthetic resin, if needed, and calcinates a carbon material and ceramic powder. A sintering process and the mixed grinding method are enforced on condition that ordinary-pressure - 200 kg/cm² at 1000-2200 degrees C. It is desirable that it is the range of 5 - 50 capacity %, as for the rate of the ceramics in the carbon / ceramic composite material used for composite-ization, it is still more desirable that it is the range of 5 - 30 capacity %, and it is desirable that it is especially the range of 10 - 20 capacity %. As for the average grain size of the electric conduction agent which consists of carbon / ceramic composite material of this invention, it is desirable that it is 0.1-10 micrometers. In order to make it a predetermined grain size, the grinder and classifier which were known well are used. For example, a mortar, a ball mill, a sand mill, a vibration ball mill, a satellite ball mill, a planet ball mill, a revolution air current type jet mill, a screen, etc. are used. At the time of trituration, wet grinding which made organic solvents, such as water or a methanol, live together can also be performed if needed. It is desirable to perform a classification in order to consider as a desired particle size. As the classification method, there is especially no limitation and it can use a screen, a pneumatic elutriation machine, etc. if needed. A classification can use dry type and wet.

[0010] the carbon / ceramic composite material of this invention -- a positive electrode -- not only a mixture but a negative electrode -- although it can add to a mixture -- a positive electrode -- the addition to a mixture is desirable 1 - 30 % of the weight is desirable, the addition to a mixture has 1 - 10 especially desirable % of the weight, and especially its 1 - 5 % of the weight is desirable, and it can be used together with electric conduction agents, such as carbon black, acetylene black, KETCHIEN black, carbon fiber metallurgy group powder (copper, nickel, aluminum, silver, etc.), a metal fiber, or a polyphenylene derivative.

[0011] The compound which can do light metal ion occlusion and discharge at amorphous negative-electrode material, a light metal, a light metal alloy, a carbonaceous compound, an inorganic oxide, inorganic chalcogenide, a metal complex, **** for organic high-molecular-compound ****. They are a carbonaceous compound and an amorphous inorganic oxide preferably. In the case of an amorphous inorganic oxide, you may use together with other negative-electrode material. It is chosen as the carbonaceous compound used as a negative-electrode material out of a natural graphite, an artificial graphite, vapor-growth carbon, the carbon with which the organic substance was calcinated. It is desirable to include graphite structure in it, even when it is small to this carbonaceous compound. For example, a natural graphite, petroleum coke, pitch coke, coal, a cresol-resin baked carbon, a furan-resin baked carbon, a polyacrylonitrile fiber baked carbon, a vapor-growth graphite, vapor-growth carbon, a mesophase pitch baked carbon, etc. are mentioned. Moreover, a different-species compound, for example, B, P, N, S, etc., may also be included in a carbonaceous compound zero to 10% of the weight besides carbon, and SiC and B₄C may also be included in it. Moreover, as inorganic chalcogenide, the sulfide which contains TiS₂, GeS, GeS₂, SnS, SnS₂, PbS, PbS₂, Sb₂S₃, Sb₂S₅, SnSiS₃, etc., for example is desirable.

[0012] As this negative-electrode material used by this invention, it is MZ-pGO-qX (it is here, the semimetal element of the 13-15th groups of a periodic table in connection with occlusion discharge of a lithium ion and transition metals of MZ being independent or ***** which consists of those combination is chalcogenide, GO(s) are the so-called amorphous mesh formation agent with being stable for making it amorphous, and a mesh ornamentation agent, and X is a fluorine). ***** in connection with lithium occlusion discharge in p expresses the mole ratio of chalcogenide, an amorphous mesh formation agent, and a mesh ornamentation agent, and it is 0.25-5.0, and ***** in connection with lithium occlusion discharge in q expresses the mole ratio of chalcogenide and a fluorine atom, and it is 0-1.0. It is raised. Furthermore, it is thought in detail that MZ offers the occlusion discharge site of a lithium at the same time it performs an oxidation-reduction reaction to the charge-and-discharge reaction time of a cell. It is thought that it is required for stabilization of a charge-and-discharge cycle to distribute stably [the occlusion discharge site of this lithium] in a medium, and pGO-qF has played the role of the dispersion medium of an occlusion discharge site. As an example of a compound of MZ, SiO, GeO, GeO₂, SnO, SnO₂, PbO, PbO₂, Pb₂O₃, Pb₂O₄, Pb₃O₄, Sb₂O₃, Sb₂O₄, Sb₂O₅, Bi₂O₃, Bi₂O₄, Bi₂O₅, VO₂, V₂O₅, MnO, Fe₂O₃, Co₂O₃, NiO, ZnO, NbO, MoO₂, MoO₃, WO₂, WO₃, GeS, GeS₂, SnS, SnS₂, PbS and PbS₂, Sb₂S₃, Sb₂S₅, SnSiS₃, etc. independently Or two or more sorts can be used together and used, and these may be multiple oxides with lithium oxides, such as Li₂SnO₂ and Li₂GeO₃, further. More preferably as MZ, it is SnO, SnO₂, SiO, and GeO, and independent ** can compound and use these. An amorphous mesh formation agent and the mesh ornamentation agent GO can mention at least one sort of oxides chosen from Si, aluminum, B, calcium, Mg, P, Li, Na, K, and V that what is necessary is just what forms an amorphous mesh with MZ. As an example of an amorphous mesh formation agent, SiO₂, aluminum 2O₃, B-2 O₃, H₃BO₃, P₂O₅, etc. can be mentioned, it is independent, or it can mix with MZ, two or more sorts can be calcinated, and amorphous negative-electrode material can be obtained. as a mesh ornamentation agent -- CaO, MgO, Li₂O, Na₂O, and K₂O etc. -- it is, and these may be added and calcinated Furthermore, introduction of F to amorphous negative-electrode material is also effective, for example, there are SnF₂, CaF₂, MgF₂, ZrF₂, etc., and these may be added and calcinated. ***** in connection with lithium occlusion discharge in p expresses the mole ratio of chalcogenide and an amorphous mesh formation agent, are 0.25-5.0, and are 0.33-2.0 more preferably. ***** in connection with lithium occlusion discharge in q expresses the mole ratio of chalcogenide and a halogen, and it is 0-1.

[0013] A more desirable compound is a compound expressed by general formula SnO-pGO with the above-mentioned compound. For example, SnO-SiO₂, SnO, 0.7SiO₂.0.2P₂O₅ and 0.1 B-2 O₃, SnO, 0.4SiO₂, 0.1aluminum2O₃, and 0.1 B-2O₃.0.3P₂O₅, SnO, 0.3 B-2O₃, 0.1CaO and 0.6P₂O₅, SnO, 0.1aluminum2O₃, 0.3 B-2O₃, 0.1MgO, 0.3P₂O₅.0.1F, etc. are mentioned.

[0014] As for the negative-electrode material of this invention, it is desirable that it is amorphous at the time of cell inclusion. It is the object which has the broadcloth dispersion band which has the peak from 20 degrees to 40 degrees with 2theta value with the X-ray diffraction method [be / amorphous] using CuK alpha rays said here, and you may have a crystalline diffraction line. Among the crystalline diffraction lines preferably looked at by 40 degrees or more 70 degrees or less with 2theta value, it is 100 or less times that they are 500 or less times of the diffraction line intensity of the peak of the broadcloth dispersion band looked at by 20 degrees or more 40 degrees or less with 2theta value desirable still more preferably, and the strongest intensity is 5 or less times especially preferably, and is not having the most desirable crystalline diffraction line.

[0015] amorphous negative-electrode material -- the calcinating method and a solution method -- it is compoundable by any method As conditions in the case of the calcinating method, 1 hour to 20 hours, with temperature fall speed have [10 degrees-C / or more //m 2000 degrees C or less and burning temperature / 500 degrees-C or more 1500 degrees C or less and a firing time] 10 degrees C [or more]/m 107 degrees C or less desirable [a programming rate]. You may cool in a firing furnace and a temperature fall is taken out out of a firing furnace again, for example, may be supplied underwater and may be cooled. Moreover, the gun method given in 217 pages (Gihodo

Shuppan Co., Ltd. 1987) of ceramic processing, the Hammer-Anvil method, the slap method, the gas atomizing method, the plasma-spraying method, a centrifugal quenching method, melt Super-quenching methods, such as the drag method, can also be used. Moreover, you may cool using the single roller method given in 172 pages (Maruzen 1991) of new glass handbooks, and a congruence roller. In the case of the material fused during baking, you may take out a baking object continuously, supplying a raw material during baking. It is desirable to agitate a melt in the case of the material fused during baking. Oxygen content is the atmosphere below 5 volume % preferably, and baking gas atmosphere is inert gas atmosphere still more preferably. As inert gas, nitrogen, an argon, helium, a krypton, a xenon, etc. are mentioned, for example.

[0016] The chemical formula of the compound which baking was carried out [above-mentioned] and obtained is computable from the weight difference of the fine particles before and behind baking as an inductively-coupled-plasma (ICP) emission-spectrochemical-analysis shortcut method as a measuring method. The average grain size of amorphous negative-electrode material has desirable 0.1-60 micrometers. In order to make it a predetermined grain size, the grinder and classifier which were known with a mortar, a ball mill, a sand mill, a vibration ball mill, the satellite ball mill, the planet ball mill, the revolution air current type jet mill, the sufficient screen, etc. are used.

[0017] Although the amounts of light metal insertion, such as a lithium to amorphous negative-electrode material, are good until it approximates them to the deposition potential of the light metal, they are desirable, for example. [400-600 mol% per negative-electrode material of] The insertion method of a light metal has the desirable electrochemical and chemical method. The method of inserting electrochemically the light metal contained in a positive active material and the method of electrochemical process of inserting directly electrochemically from a light metal or its alloy are desirable. The chemical method has mixture with a light metal, contact or an organic metal, for example, a butyl lithium etc., and the method of making it react. Especially this light metal has a lithium or a desirable lithium ion.

[0018] The positive active materials used by this invention are occlusion and the compound which can be emitted about light metal ion, for example, are a transition-metals oxide and transition-metals chalcogenide. A transition-metals oxide is desirable and the transition-metals oxide containing especially a lithium is desirable.

[0019] As desirable transition metals used by this invention, Ti, V, Cr, Mn, Fe, Co, nickel, Cu, Nb, Mo, and W can be mentioned, and manganese dioxide, a vanadium pentoxide, an iron oxide, a molybdenum oxide, a molybdenum sulfide, cobalt oxide, an iron sulfide, a titanium sulfide, etc. are desirable in the compound of these transition metals. These compounds are independent, or two or more sorts can be used together and used for them. Moreover, it can use together with the transition-metals oxide containing the lithium described below, and can also use.

[0020] The transition-metals oxide containing a lithium is [after mixing a lithium compound and a transition-metals compound] compoundable by calcinating. Hereafter, a lithium compound and a transition-metals compound are explained in full detail.

[0021] As a desirable lithium compound used by this invention, a lithium hydroxide, a lithium carbonate, a lithium nitrate, lithium sulfate, a sulfurous-acid lithium, a phosphoric acid lithium, a tetraboric acid lithium, a chloric-acid lithium, a lithium perchlorate, a thiocyanic-acid lithium, a formic acid lithium, an acetic-acid lithium, an oxalic acid lithium, a lithium citrate, a lactic-acid lithium, a tartaric-acid lithium, a pyruvic-acid lithium, a trifluoromethane sulfonic-acid lithium, a 4 boron acid lithium, a 6 fluoridation phosphoric acid lithium, a lithium fluoride, a lithium chloride, a lithium bromide, and a lithium iodide can

[0022] As a transition-metals compound, the transition-metals oxide of univalent - 6 **, this transition-metals salt, and this transition-metals complex salt can be used. As transition metals, Ti, V, Cr, Mn, Fe, Co, nickel, Cu, Nb, Mo, and W can be mentioned. A compound given [as these transition-metals compounds] in the paragraphs 0008 and 0009 of JP,6-243897,A, The lithium compound of VOd (d=2-2.5) and VOd, ammonium metavanadate, MnO₂, Mn₂O₃, manganese hydroxide, manganese carbonate, manganese nitrate, An iron oxide (2 trivalent), a tri-iron tetraoxide, iron-hydroxide (2 trivalent) iron acetate (2 trivalent), Citric-acid iron (2 trivalent), a ferric ammonium citrate (2 trivalent), oxalic acid iron (2 trivalent), Oxalic acid iron ammonium (2 trivalent), CoO and Co₂O₃, Co₃O₄, LiCoO₂, cobalt carbonate, Basic cobalt carbonate, cobalt hydroxide, a cobalt sulfate, a cobalt nitrate, Nickel oxide, nickel hydroxide, nickel carbonate, basic nickel carbonate, A nickel sulfate, nickel nitrate, a nickel acetate, oxysalt-ized niobium, 5 chlorination niobium, 5 iodation niobium, 1 niobium oxide, 2 niobium oxides, 3 niobium oxides, 5 niobium oxides, Oxalic acid niobium, a niobium methoxide, niobium ethoxide, niobium propoxide, Niobium butoxide, a lithium niobate, MoO₃ and MoO₂, LiMo₂O₄, a molybdenum pentachloride, An ammonium molybdate, a lithium molybdate, molybdo ammonium phosphate, molybdenum-oxide acetylacetonato, WO₂ and WO₃, a tungstic acid, tungstic-acid ammonium, wolframophosphoric-acid ammonium, etc. are raised. independent in these -- or two or more sorts can be used together

[0023] The compound given [as an especially desirable transition-metals compound] in the paragraphs 0010 and 0011 of JP,6-243897,A used by this invention and MoO₃ and MoO₂, LiMo₂O₄, and WO₂ and WO₃ are raised.

[0024] The desirable positive active material used by this invention is a transition-metals oxide containing the lithium expressed with Li_xMyO_z (it is at least one sort chosen from M=V, and Mn, Fe, Co and nickel here a subject, $x=0.05-1.2$, $y=1$ or 2, and $z=1.5-5$).

Moreover, alkali metal other than a lithium, alkaline earth metal, transition metals other than Above M, or the periodic-table IIIB-V group B (aluminum, Ga, In, Si, germanium, Sn, Pb, Sb, Bi) may also be included in these. Moreover, P, B, etc. may also be included.

[0025] As a still more desirable lithium content metallic-oxide positive active material used by this invention Li_xCoO_2 , Li_xNiO_2 , $\text{Li}_x\text{CoNi}_{1-a}\text{O}_2$, $\text{Li}_x\text{CoV}_{1-b}\text{O}_2$, $\text{Li}_x\text{CoFe}_{1-b}\text{O}_2$, $\text{Li}_x\text{Mn}_2\text{O}_4$, Li_xMnO_2 , $\text{Li}_x\text{Mn}_2\text{O}_3$, $\text{Li}_x\text{MnCo}_2\text{-bO}_2$, $\text{Li}_x\text{MnNi}_2\text{-bO}_2$, $\text{Li}_x\text{MnV}_2\text{-bO}_2$, and $\text{Li}_x\text{MnFe}_{1-b}\text{O}_2$ (it is $x=0.05-1.2$, $a=0.1$ to 0.9, $b=0.8$ to 0.98, and $z=1.5-5$ here) are raised.

[0026] As most desirable lithium content transition-metals oxide positive active material used by this invention, Li_xCoO_2 , Li_xNiO_2 , $\text{Li}_x\text{CoNi}_{1-a}\text{O}_2$, $\text{Li}_x\text{Mn}_2\text{O}_4$, and $\text{Li}_x\text{CoV}_{1-b}\text{O}_2$ (it is $x=0.05-1.2$, $a=0.1$ to 0.9, $b=0.9$ to 0.98, and $z=2.02-2.3$ here) are raised.

[0027] Although the positive active material used by this invention is compoundable with the method and solution reaction which are calcinated after mixing a lithium compound and a transition-metals compound with dry type or wet, especially its calcinating method is desirable. Although 350-1500 degrees C of burning temperature are desirable, after carrying out temporary quenching at further 250-900 degrees C, it is desirable to carry out actual baking at 350-1500 degrees C. 2 - 20 hours of a firing time are desirable, and after calcinating, you may anneal it at 200-900 degrees C further. baking gas atmosphere -- an oxidizing atmosphere and reducing atmosphere -- all can be taken For example, the gas which prepared the oxygen density in arbitrary proportion among air or hydrogen, a carbon monoxide, nitrogen, an argon, helium, a krypton, a xenon, a carbon dioxide, etc. are mentioned.

[0028] As for the average grain size of the positive active material used by this invention, it is desirable that the volume of a 0.5-30-micrometer particle is 95% or more. Although not limited especially as a specific surface area, 0.01-50m²/g is desirable at a BET

adsorption method. In order to make it a predetermined grain size, the grinder and classifier which were known well are used. For example, a mortar, a ball mill, a vibration ball mill, a vibration mill, a satellite ball mill, a planet ball mill, a revolution air current type jet mill, a screen, etc. are used. As for supernatant pH when using it, after washing the positive active material obtained by baking by water, acid solution, alkaline solution, and the organic solvent, and mixing 5g of positive active materials with 100ml of distilled water, six to about 11 are desirable.

[0029] It can cover with an oxide with a chemical formula which is different from the positive active material used or a negative-electrode active material in the positive active material of the oxide used by this invention, or the front face of negative-electrode material. This scaling object has a desirable oxide containing the compound which dissolves also acid and alkaline. A metallic oxide with still higher electronic-conduction nature is desirable. PbO_2 , Fe_2O_3 , and SnO_2 and In_2O_3 , ZnO , etc. -- or it is desirable to include dopants (for example, a metal, a halogen, etc. from which a valence differs in an oxide) in these oxides [for example,] It is SiO_2 , SnO_2 , Fe_2O_3 , and ZnO and PbO_2 especially preferably. The amount of the metallic oxide used for such surface treatment has 0.1 - 10 desirable % of the weight per this positive active material and negative-electrode material, especially its 0.2 - 5 % of the weight is desirable, and its 0.3 - 3 % of the weight is the most desirable.

[0030] Moreover, in addition to this, the front face of a positive active material or negative-electrode material can be reformed. For example, processing by processing, the conductive polymer, the polyethylene oxide, etc. by processing and the chelating agent is mentioned by the esterification agent in the front face of a metallic oxide.

[0031] As a binder, kinds or such mixture can be used for the polymer which has polysaccharide, thermoplastics, and rubber elasticity. As a desirable example, starch, polyvinyl alcohol, a carboxymethyl cellulose, hydroxypropylcellulose, a regenerated cellulose, a diacetyl cellulose, polyvinyl chloride, a polyvinyl pyrrolidone, a polytetrafluoroethylene, a polyvinylidene fluoride, polyethylene, polypropylene, an ethylene-propylene-diene terpolymer (EPDM), sulfonation EPDM, styrene butadiene rubber, a polybutadiene, a fluororubber, and a polyethylene oxide can be mentioned. Moreover, when using like polysaccharide a lithium and the compound containing a functional group which reacts, it is desirable to add a compound like an isocyanate machine and to make the functional group deactivate. The addition of the binder has 2 - 30 desirable % of the weight. a mixture -- the distribution of an inner binder -- homogeneity -- even when -- an ununiformity is sufficient

[0032] In the constituted cell, a filler can be used anything, if it is the fibrous material which does not cause a chemical change. Usually, fiber, such as olefin system polymer, such as polypropylene and polyethylene, glass, and carbon, is used. Although especially the addition of a filler is not limited, 0 - 30 % of the weight is desirable.

[0033] The object known as an inorganic and organic solid electrolyte can be used for an ion electric conduction agent, and it is indicated by the term of the electrolytic solution for details. A pressure reinforcement agent is a compound which raises the below-mentioned internal pressure, and a carbonate is an example of representation.

[0034] Generally the electrolyte consists of a solvent and lithium salt (an anion and lithium cation) dissolved in the solvent. As a solvent, propylene carbonate, ethylene carbonate, butylene carbonate, Dimethyl carbonate, diethyl carbonate, methylethyl carbonate, Gamma-butyrolactone, methyl formate, methyl acetate, 1, 2-dimethoxyethane, A tetrahydrofuran, 2-methyl tetrahydrofuran, dimethyl sulfoxide, 1, 3-dioxolane, a formamide, a dimethylformamide, a dioxolane, An acetonitrile, a nitromethane, an ethyl monochrome glyme, trialkyl phosphate, Trimethoxy methane, a dioxolane derivative, a sulfolane, 3-methyl-2-oxazolidinone, Non-proton nature organic solvents, such as propylene carbonate derivative, tetrahydrofuran derivative, ethyl ether, 1, and 3-propane ape ton, can be mentioned, and these kinds or two sorts or more are mixed and used. As a cation of the lithium salt dissolved in these solvents For example, ClO_4^- , BF_4^- , PF_6^- , CF_3SO_3^- , CF_3CO_2^- , AsF_6^- , SbF_6^- , 2 $(\text{CF}_3\text{SO}_2)\text{N}^-$, $\text{B}_{10}\text{Cl}_{10}^{2-}$, (1, 2-dimethoxyethane) The anion of 2ClO_4^- , low-grade aliphatic carboxylic-acid ion, AlCl_4^- , Cl^- , Br^- , I^- , and a chloro borane compound and 4 phenyl boric-acid ion can be mentioned, and these kinds or two sorts or more can be used. It is desirable to include annular carbonate and/or un-annular carbonate especially. For example, it is desirable to include diethyl carbonate, dimethyl carbonate, and methylethyl carbonate. Moreover, it is desirable to include ethylene carbonate and propylene carbonate. Moreover, the electrolyte which contains LiCF_3SO_3 , LiClO_4 and LiBF_4 and/or LiPF_6 in the electrolytic solution which mixed suitably the propylene carbonate, 1, 2-dimethoxyethane, dimethyl carbonate, or diethyl carbonate other than ethylene carbonate is desirable. In those supporting electrolytes, especially the thing for which LiPF_6 is included is desirable.

[0035] although especially the amount that adds these electrolytes in a cell is not limited -- a positive active material, the amount of negative-electrode material, and the size of a cell -- **** for initial complements -- things are made Although especially the concentration of a supporting electrolyte is not limited, its 0.2-3 mols per 1l. of electrolytic solutions are desirable.

[0036] Moreover, a solid electrolyte can be used together to the electrolytic solution. It is divided into an inorganic solid electrolyte and an organic solid electrolyte as a solid electrolyte. The nitride of Li, the halogenide, the oxygen-acid salt, etc. are well known by the inorganic solid electrolyte, for example, Li_3N , LiI , Li_5NI_2 , $\text{Li}_3\text{N-LiI-LiOH}$, Li_4SiO_4 , $\text{Li}_4\text{SiO}_4\text{-LiI-LiOH}$, $\text{xLi}_3\text{PO}_4\text{-(1-x) Li}_4\text{SiO}_4$, Li_2SiS_3 , a phosphorus-sulfide compound, etc. are mentioned to it. The macromolecule matrix material which made the polymer which contains the polymer, the polypropylene oxide derivative, or this derivative containing a polyethylene-oxide derivative or this derivative as an example of an organic solid electrolyte, the polymer containing an ionic dissociation machine, the polymer containing an ionic dissociation machine, the mixture of the above-mentioned non-proton nature electrolytic solution and phosphoric ester polymer, and the non-proton nature polar solvent contain is mentioned. Furthermore, there is also the method of adding a polyacrylonitrile to the electrolytic solution. Moreover, how to use inorganic and an organic solid electrolyte together is also learned.

[0037] Moreover, you may add other compounds to an electrolyte for the purpose which improves electric discharge and a charge-and-discharge property. For example, a pyridine, a triethyl force fight, a triethanolamine, Cyclic ether, ethylenediamine, n-glyme, hexalin acid TORIAMIDO, A nitrobenzene derivative, sulfur, a quinonimine dye, N-substitution oxazolidinone, and N and N'-substitution imidalidinone, Ethylene glycol dialkyl ether, quarternary ammonium salt, a polyethylene glycol, A pyrrole, a 2-methoxyethanol, AlCl_3 , the monomer of a conductive polymer electrode active material, The triethylenephosphoramidate, trialkylphosphine, a morpholine, An aryl compound, the crown ethers like 12-crown 4 and hexamethylphosphoric triamide and 4-alkyl morpholine with a carbonyl group, the bicyclic third class amine, oil, the fourth class phosphonium salt, the third class sulfonium salt, etc. can be mentioned.

[0038] Moreover, in order to make the electrolytic solution into incombustibility, a ** halogen solvent, for example, a carbon tetrachloride, and a 3 fluoridation ethylene chloride can be included in the electrolytic solution. Moreover, in order to give fitness to elevated-temperature preservation, carbon dioxide gas can be included in the electrolytic solution.

[0039] As a separator, it has big ion transmittance, and has a predetermined mechanical strength, and an insulating fine porosity thin film is used. Moreover, it is desirable to have the function to blockade a hole above 80 degrees C and to raise resistance. The sheet and nonwoven

fabric which were built with olefin system polymer or glass fibers, such as organic-solvent-proof nature, a hydrophobic shell poly pre pyrene, and/or polyethylene, etc. are used. The range for which the aperture of a separator is generally used as a separator for cells is used. For example, 0.01-10 micrometers is used. Generally the thickness of separator is used in the range of the separator for cells. For example, 5-300 micrometers is used. Manufacture of a separator is [but] good as how to make a hole after composition of polymer also in dry type, the extending method or a solution, solvent removal methods, or those combination.

[0040] If it is the electronic-conduction object which does not cause a chemical change in the constituted cell as a charge collector of positive and a negative electrode, it is good anything. For example, the thing which made carbon, nickel, titanium, or silver process is used for the front face of aluminum or stainless steel else [, such as stainless steel, nickel, aluminum, titanium, and carbon] as a material in a positive electrode. Especially, aluminum or an aluminium alloy is desirable. The thing which made the front face of copper or stainless steel else [, such as stainless steel, nickel, copper, titanium, aluminum, and carbon] process carbon, nickel, titanium, or silver, an aluminum-Cd alloy, etc. are used for a negative electrode as a material. Especially, copper or a copper alloy is desirable. Oxidizing the front face of such material is also used. Moreover, it is desirable to attach irregularity to a current collection body surface with surface treatment. As for a configuration, a film besides the foil, a sheet, the thing netted and punched, a lath object, a porosity object, a foam, the Plastic solid of a fiber group, etc. are used. Although especially thickness is not limited, a 1-500-micrometer thing is used.

[0041] The configuration of a cell can apply coin, a button, a sheet, a cylinder, flatness, an angle, etc. to all. The configuration of a cell is compressed into the configuration of a pellet at the time of coin or a button, and the mixture of a positive active material or negative-electrode material is mainly used. The thickness and the diameter of the pellet are decided with the size of a cell. Moreover, when the configurations of a cell are a sheet, a cylinder, and an angle, on a charge collector, the mixture of a positive active material or negative-electrode material is applied, (coat) dried and compressed, and is mainly used. Common practice can be used for the method of application. For example, the reverse rolling method, the direct rolling method, the blade method, the knife method, the extrusion method, the curtain method, the gravure method, the bar method, the dipping method, and the squeeze method can be mentioned. The blade method, the knife method, and the extrusion method are desirable also in it. As for an application, it is desirable to carry out the speed for 0.1-100m/. Under the present circumstances, according to the solution physical properties of a mixture, and a drying property, the surface state of a good application layer can be obtained by selecting the above-mentioned method of application. The time of one side [every] ** or double-sided **** is sufficient as an application. Moreover, continuation, an intermission, or a stripe is sufficient as an application. Although the thickness, length, and width of the application layer are decided with the size of a cell, the thickness of the application layer of one side is in the state where it was compressed after dry, and especially its 1-2000 micrometers are desirable.

[0042] The method generally adopted can be used as a pellet, or dryness of a sheet or the dehydration method. Especially, it is desirable independent or to combine and to use hot blast, a vacuum, infrared radiation, far infrared rays, an electron ray, and a damp wind. The range of temperature of 80-350 degrees C is desirable, and its range which is 100-250 degrees C is especially desirable. moisture content -- the cell whole -- 2000 ppm or less -- desirable -- a positive electrode -- a mixture and a negative electrode -- it is desirable to make it 500 ppm or less in a mixture or an electrolyte, respectively in respect of cycle nature Although the method generally adopted can be used for a pellet or the method of pressing a sheet, a die-press method and its calender pressing method are especially desirable. Although especially press ** is not limited, its 0.2 - 3 t/cm2 is desirable. The press speed of the calender pressing method has the amount of desirable 0.1-50m/, and press temperature has desirable room temperature -200 degree C. As for the ratio of negative-electrode sheet width of face to a positive-electrode sheet, 0.9-1.1 are desirable, and 0.95-especially 1.0 are desirable. the content ratio of a positive active material and negative-electrode material -- a compound kind and a mixture -- since it changes with prescription, although it cannot limit, it can be set as the optimal value in the viewpoint of capacity, cycle nature, and safety

[0043] this -- a mixture -- after rolling or folding those sheets after piling up through a sheet and a separator, inserting them in a can and connecting a sheet with a can electrically, they pour in the electrolytic solution and form a cell can using an obturation board At this time, a relief valve can be used as an obturation board. It may be equipped with the various safe elements known from the former besides a relief valve. For example, a fuse, bimetal, a PTC element, etc. are used as an overcurrent-protection element. Moreover, the method of making a cut in a cell can, the gasket crack method, the obturation board crack method, or cutting process with a lead board can be used for everything but a relief valve as a cure of internal pressure elevation of a cell can. Moreover, the protection network which built the surcharge and the cure against an overdischarge into the battery charger may be made to provide, or you may make it connect independently. Moreover, the method which intercepts current by elevation of cell internal pressure can be provided as a cure against overcharge. At this time, the compound which raises internal pressure can be included in a mixture or an electrolyte. as the example of the compound used in order to raise internal pressure -- Li2 -- carbonates, such as CO3, LiHCO3, Na2CO3, and NaHCO3, CaCO3, MgCO3, etc. can be mentioned

[0044] A metal and an alloy with electrical conductivity can be used for a can or a lead board. For example, metals or those alloys, such as iron, nickel, titanium, chromium, molybdenum, copper, and aluminum, are used. A well-known method (electric welding of an example, a direct current, or an alternating current, laser welding, ultrasonic welding) can be used for the welding process of a cap, a can, a sheet, and a lead board. The compound and mixture which are known from the former, such as asphalt, can be used for the sealing compound for obturation.

[0045] Although not limited to especially the use of the non-water rechargeable battery of this invention, when it carries in electronic equipment, for example, A color notebook computer, monochrome notebook computer, a subnote PC pen input personal computer, A pocket (palm top) personal computer, a note type word processor, a pocket word processor, an Electronic Book player, a cellular phone, and a cordless phon -- a cordless handset and a pager -- A handy terminal, pocket facsimile, a pocket copy, a pocket printer, A headphone stereo, a video movie, a liquid crystal television, a handy cleaner, Portable CD, a mini disc, an electric shaver, an electronic translating machine, a car telephone, a transceiver, a power tool, an electronic notebook, a calculator, memory card, a tape recorder, radio, a backup power supply, memory card, etc. are mentioned. In addition, an automobile, electric vehicles, a motor, lighting fitting, a toy, a game machine machine, a load conditioner, an iron, a clock, a stroboscope, a camera, medical equipment (a pacemaker, a hearing-aid, shoulder Japanese fir machine, etc.), etc. are mentioned as a noncommercial use. Furthermore, it can use as the various objects for munitions, and an object for space. Moreover, it is also combinable with other rechargeable batteries, or a solar battery or a primary cell.

[0046] Although a desirable combination of this invention has a desirable combination, an above-mentioned chemistry material and an above-mentioned cell component part As an amorphous negative-electrode material, especially SnO-SiO2, SnO and 0.2 B-2O3.0.2P2O5, SnO, 0.2SiO2, and 0.2 B-2O3.0.2P2O5, SnO, 0.5P2O5, 0.2aluminum2O3, 0.2 B-2O3 and 0.1MgO, SnO, 0.5P2O5, 0.2aluminum2O3, 0.2 B-2O3.0.1F, etc. as a positive active material As LixCoO2, LixNiO2, LixMnO2, at least one sort of compounds chosen from LixMn 2O4

(it is $x=0.05-1.2$ here), and carbon / ceramic composite material, C(JSP:Japan graphite)/B4 C/SiC=79/4/17 (vol%), C/B4 C/WB=65/25/10 (vol%), C/B4 C/ZrB₄=70/20/10 (vol%), It is desirable to use carbon materials, such as acetylene black and a graphite, as C/SiO₂=75 / 25 (vol%), C/Si₃N₄=84/16 (vol%), and a combined use electric conduction agent. The positive-electrode charge collector is carrying out configurations, such as the network and sheet which are made from stainless steel or aluminum, a foil, and a lath. The negative-electrode charge collector is carrying out configurations, such as the network and sheet which are made from stainless steel or copper, a foil, and a lath. a binder is independent in elastomers, such as polymer containing fluorine-containing thermoplasticity compounds, such as a polyvinylidene fluoride and poly fluoro ethylene, and an acrylic acid, styrene butadiene rubber, and an ethylene propylene terpolymer, -- or it can mix and use Moreover, it is still more desirable as the electrolytic solution ethylene carbonate and to mix lithium salt, such as LiBF₄ and LiCF₃SO₃, further including LiPF₆, and to use as the combination of ester compounds, such as annular [, such as diethyl carbonate and dimethyl cull BONETO,], un-annular carbonate, or ethyl acetate, and a supporting electrolyte. Furthermore, independent or those combination of polypropylene or polyethylene are desirable as a separator. Any of coin, a button, a cylinder, flatness, and a square shape are sufficient as the gestalt of a cell. It is desirable to equip a cell with a means (an example, an internal pressure open-sand-mold relief valve, a current interception type relief valve, separator that raises resistance at an elevated temperature) by which safety is securable also for a malfunction.

[0047]

[Example] Although an example is raised to below and this invention is explained in more detail, unless the main point of invention is exceeded, this invention is not limited to an example.

[0048] Synthetic example Baking **SnO-SiO₂ (compound A) of amorphous negative-electrode material

SnO13.5g and SiO₂ 6.0g were blended dryly, it put into the crucible made from an alumina, and the temperature up was carried out to 1000 degrees C by part for bottom 10-degree-C/ of argon atmosphere. After calcinating at 1000 degrees C for 12 hours, the temperature was lowered to the room temperature by part for 6-degree-C/. The crucible made from an alumina was taken out from the firing furnace, the Seishin Enterprise jet mill ground the glass of the light yellow transparence in a crucible after coarse grinding, and **** of 5micro of mean particle diameters was obtained (compound A). The amorphous thing for which Compound A measures crystallinity with the X-ray diffraction method which used Cu-K alpha rays, has the broadcloth dispersion band which has the peak in the range of 20 degrees - 40 degrees with 2theta value, and does not have a crystalline diffraction line was checked. Si content dissolves the compound A which carried out weighing capacity in 18 N:H₂SO₄/6 N:HCl=1 / 2 (capacity factor) among the chemical compositions of Compound A. Computing from the weight of the insoluble section which separated, and Si content for which it asked from the atomic absorption spectrum, it computed by M/100:EDTA by having carried out the chelatometry of the sample which diluted the aforementioned acid fusible part 20 times using distilled water, and it checked Sn/Si=1/1 substantially. The content of divalent Sn in Compound A is the sample which dissolved compound A0.2g which carried out weighing capacity in the mixture of 18 N:H₂SO₄3ml, 6 N:HF5ml, and N/10:K₂Cr₂O₇ 25ml N/10:Na₂S₂O₃ It computed by having carried out the oxidation reduction titration, and checked that it was 98% or more of Sn.

** SnO, 0.6SiO₂, 0.1aluminum₂O₃, and 0.1 B-2O₃.0.2P₂O₅ (compound B)

SnO13.5g, SiO₂ 3.6g, aluminum₂O₃1.0g, B-2O₃0.7g, and P₂O₅2.8g were blended dryly, it put into the crucible made from an alumina, and the temperature up was carried out to 1000 degrees C by part for bottom 10-degree-C/ of argon atmosphere. After calcinating at 1000 degrees C for 12 hours, the temperature was lowered to the room temperature by part for 6-degree-C/. The crucible made from an alumina was taken out from the firing furnace, the Seishin Enterprise jet mill ground the glass of the light yellow transparence in a crucible after coarse grinding, and **** of 5micro of mean particle diameters was obtained (compound B). By crystalline evaluation by the X-ray diffraction method which used Cu-K alpha rays, it checked that Compound B was amorphous like Compound A. Compound B checked by performing chemical-composition evaluation like Compound A except having computed aluminum, B, and P content from the atomic absorption method. Moreover, it checked that the content of divalent Sn in Compound B was 98% or more of Sn.

[0049] The compounds A and B adjusted above as a negative-electrode material, As a positive active material LiCoO₂, carbon/charge of ceramic composite X [C(JSP:Japan graphite)/B4 C/SiC=79/4/17 (vol%)], and the cylinder cell using Y [C(JSP:Japan graphite)/B4 C/ZrB₂=70/20/10 (vol%)] are created by the following method. 40-degree C cycle nature was evaluated.

[0050] As an example-1 negative-electrode material, compound A86% of the weight of the synthetic example, it mixed as an electric conduction agent at a rate of 6 % of the weight of scale-like graphites, and 3 % of the weight of acetylene black, 4 % of the weight and 1 % of the weight of carboxymethyl celluloses were further added for the water distribution object of poly fluoride kinky thread NIDEN as a binder, water was kneaded as a medium, and the slurry was produced. This slurry was applied to both sides of copper foil with a thickness of 18 micrometers by the extrusion method, and carried out compression molding with the calender press machine after dryness, it cut to predetermined width of face and length, and the band-like negative-electrode sheet was produced. The thickness of a negative-electrode sheet was 124 micrometers. The slurry which added carbon / ceramic composite material X as an electric conduction agent 87% of the weight, added 3 % of the weight of polytetrafluoroethylene water distribution objects and 1 % of the weight of sodium polyacrylate as a binder, further 6 % of the weight and 3 % of the weight of acetylene black, kneaded water as a medium as a positive-electrode material, and was obtained was applied by the method same to both sides of an aluminum foil with a thickness of 20 micrometers as the above, it dried, LiCoO₂ was pressed, it cut, and the 220-micrometer band-like positive-electrode sheet was produced. The above-mentioned negative-electrode sheet and a positive-electrode sheet are each the dew-point after carrying out spot welding of the lead board of nickel and aluminum to an edge, respectively. - Dehydration dryness was carried out in dry air 40 degrees C or less for 150-degree-C 2 hours. Furthermore, the laminating was carried out in the order of a dried [dehydration] positive-electrode sheet (5) fine porosity polypropylene film separator (Celgard 2400), a dried [dehydration] negative-electrode sheet (4), and a separator (3), this was involved in, and it wound in the shape of a whorl by the opportunity.

[0051] It contained with the iron closed-end cylindrical cell can (2) which performed nickel plating which serves this winding object as a negative-electrode terminal. Per [1L / LiPF₆ and LiBF₄] were poured into 0.9, respectively, 0.1 mols were contained and the electrolyte with which a solvent consists of 2:2:6 capacity mixed liquor of ethylene carbonate, butylene carbonate, and dimethyl carbonate was poured into the cell can. the cell lid which has a positive-electrode terminal -- a gasket (1) -- minding -- the cylindrical cell was produced in total In addition, the positive-electrode terminal (8) connected beforehand the positive-electrode sheet (5) and the cell can (2) with the negative-electrode sheet (4) by the lead terminal. The cross section of a cylindrical cell was shown in drawing 1 . In addition, (7) is a relief valve. The cylindrical cell was similarly manufactured except having changed the negative-electrode material A, and carbon and the ceramic composite material X into the compound given in Table 1. Charge-and-discharge conditions were made into 4.3-2.7V, and 1 mA/cm². The result was shown in the following table 1.

[0052] As shown in example -2 table 1, carbon / ceramic composite-material X ** uses [the electric conduction agent of a negative-electrode sheet] 6 % of the weight and 3 % of the weight of acetylene black for Y, and it is an example as an electric conduction agent of a positive-electrode sheet further except use **** in 6 % of the weight of phosphorus flaky graphites, and 3 % of the weight of acetylene black. - Using the cylindrical cell manufactured like 1, it is 4.3-2.7V, and 1 mA/cm2 charge-and-discharge conditions, and 40-degree C cycle nature was evaluated. The result was shown in the following table 1.

[0053] As shown in example -3 table 1, carbon / ceramic composite-material X ** Y for the electric conduction agent of a negative-electrode sheet 6 % of the weight, 3 % of the weight of acetylene black is used. carbon / ceramic composite-material X ** further Y for the electric conduction agent of a positive-electrode sheet And 6 % of the weight, And it is an example except having used 3 % of the weight of acetylene black. - Using the cylindrical cell manufactured like 1, 4.3-2.7V, and 1 mA/cm2 charge-and-discharge conditions estimated 40-degree C cycle nature, and the result was shown in the following table 1.

[0054] It is an example about the cylindrical cell which a negative-electrode sheet is created like the example example -1 of comparison, and the electric conduction agent of a positive-electrode sheet consists only of 6 % of the weight of phosphorus flaky graphites, and 3 % of the weight of acetylene black, and does not contain carbon / ceramic composite material. - It manufactured like 1, and it is 4.3-2.7V, and 1 mA/cm2 charge-and-discharge conditions, and 40-degree C cycle nature was evaluated. the result -- No. -- it was shown in the following table 1 as 13 and 14 (example of comparison)

[0055]

Explanation of a cable address a; negative-electrode material (compounds A and B)

b; electric conduction agent (carbon / ceramic composite material : X, Y, phosphorus flaky-graphite:G, acetylene black : AcB)

c; service capacity (per [mAh] 1g of negative-electrode material)

d; 40-degree-C cycle nature (the number of cycles which becomes 75 with a 25-degree-C capacity [1st]%)

[0056]

[Table 1]

表 1

No.	a 負極 材料	b 導電剤		c 容量 (mAh/g)	d サイクル 性 (回)	備考
		負極シート：重量%	正極シート：重量%			
1	A	G : 6 , AcB : 3	X : 6 , AcB : 3	504	330	実施例 1
2	A	" , "	Y : 6 , "	508	345	"
3	B	" , "	X : 6 , "	480	360	"
4	B	" , "	Y : 6 , "	494	353	"
5	A	X : 6 , "	G : 6 , AcB : 3	514	267	実施例 2
6	A	Y : 6 , "	" , "	498	285	"
7	B	X : 6 , "	" , "	481	304	"
8	B	Y : 6 , "	" , "	473	296	"
9	A	X : 6 , "	X : 6 , "	521	324	実施例 3
10	A	Y : 6 , "	Y : 6 , "	514	353	"
11	B	X : 6 , "	X : 6 , "	501	369	"
12	B	Y : 6 , "	Y : 6 , "	488	386	"
13	A	G : 6 , AcB : 3	G : 6 , AcB : 3	502	226	比較例
14	B	" , "	" , "	487	244	"

[0057] sample No.1-12 using the carbon / ceramic (carbide, way ghost) composite material of this invention as an electric conduction agent -- No. of the example of comparison -- compared with 13 and 14, capacity excels [at the cycle property of 40 degrees C] above equivalent and is desirable Furthermore, as well as sample No.1-12 when carbon / ceramic (oxide, nitride) composite material was used as an electric conduction agent, improvement with a cycle property of 40 degrees C was accepted.

[0058]

[Effect of the Invention] Like this invention, if carbon / ceramic composite material is used as a kind of electric conduction agent at least, the non-water rechargeable battery with which the charge-and-discharge cycle property of 40 degrees C has been improved notably can be obtained.

[Translation done.]